288. The Photoelectron Spectra of D_{2d} and C_{2v} Hydrocarbons Containing Two Norbornadiene or Quadricylane Groups

by **Branka Kovač**[1][2], **Edgar Heilbronner**[1], **Horst Prinzbach**[3] and **Klaus Weidmann**[3]

Physikalisch-chemisches Institut der Universität Basel, Klingelbergstrasse 80, CH-4056 Basel

Lehrstuhl für Organische Chemie der Universität Freiburg i. Br., Albertstrasse 21, D-7800 Freiburg i. Br.

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Summary

The photoelectron spectra of the hydrocarbons **1** to **4** have been recorded and interpreted by qualitative correlation with the spectra of their subsystems norbornadiene, quadricyclane, allene and cyclopropane.

It has been shown that the interactions of the symmetry adapted orbitals of the subsystems are governed not only by their symmetry behaviour with respect to D_{2d} in **1** and **2**, or C_{2v} in **3** and **4**, but also by the local symmetry at the points of attachment of the subsystems.

Conjugation and/or homoconjugation between two-centre π-orbitals and/or *Walsh*-orbitals in polycyclic hydrocarbons have been studied extensively by photoelectron spectroscopy, under the implicit assumption of the applicability of *Koopmans'* approximation [1].

In this note we discuss the photoelectron spectra of the following hydrocarbons:

1: Bis(7-norbornadienylidene)methane,

2: Bis(7-quadricyclanylidene)methane,

3: Dispiro[bicyclo[2.2.1]hepta-2,5-diene-7,1'-cyclopropane-2',7''-bicyclo[2.2.1]-hepta-2'',5''-diene],

4: Dispiro[tetracyclo[3.2.0.0^{2,7}0^{4,6}]heptane-3,1'-cyclopropane-2',3''-tetracyclo-[3.2.0.0^{2,7}0^{4,6}]heptane],

which are shown in *Figures 1* and *2*. The compounds **1** to **4** are of interest in connection with investigations of the photochemical behaviour of polychromophoric systems [2]. (This aspect will be discussed in a later contribution). The compounds have been prepared from bisquadricyclanylidene [3], or its dichlorocarbene adduct, according to conventional methods [4].

From a photoelectron spectroscopic point of view, these rather large hydrocarbons are noteworthy because two of them, **1** and **2**, are highly symmetric, belonging to the not too common group D_{2d}, whereas **3** and **4** are of C_{2v} symmetry. As a consequence, the outer valence orbitals are (almost) entirely symmetry condi-

[1] Basel.

[2] Permanent Address: 'Ruđer Bošković' Institute, 41001 Zagreb, Croatia, Yugoslavia.

[3] Freiburg i. Br.

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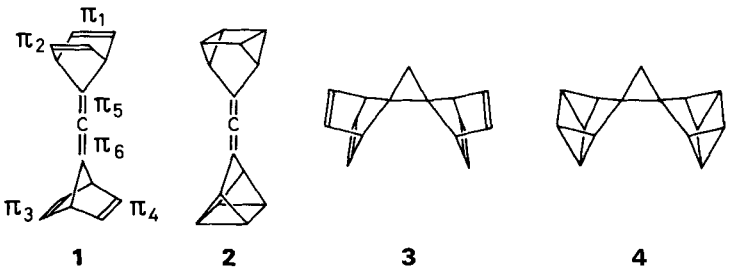


tioned, so that a rather straightforward assignment of the photoelectron spectra can be performed by correlation with the spectra available for their subsystems, *i.e.* norbornadiene, quadricyclane, allene and cyclopropane.

Hydrocarbon 1. – For a qualitative discussion of the first bands in the photoelectron spectrum of **1** (symmetry D_{2d}) we need only consider those outer valence shell orbitals which are of pure π-parentage. With reference to the numbering of the basis two-centre π-orbitals π_μ shown in formula **1** we define the phase relationship of π_1, π_2, π_3 and π_4 in such a way that they transform into each other according to the totally symmetric irreducible representation A_1 of the group D_{2d}. By necessity, π_5 and π_6 span the degenerate representation E. Thus the symmetry adapted π-orbitals of **1** are:

$$\begin{aligned} a_1 &= (\pi_1+\pi_2+\pi_3+\pi_4)/2 = (\pi_S^u+\pi_S^l)/\sqrt{2} \\ b_2 &= (\pi_1+\pi_2-\pi_3-\pi_4)/2 = (\pi_S^u-\pi_S^l)/\sqrt{2} \\ e(nBD) &= \begin{cases} (\pi_1-\pi_2+\pi_3-\pi_4)/2 = (\pi_A^u+\pi_A^l)/\sqrt{2} \\ (\pi_1-\pi_2-\pi_3+\pi_4)/2 = (\pi_A^u-\pi_A^l)/\sqrt{2} \end{cases} \\ e(All) &= \begin{cases} (\pi+\pi_6)/\sqrt{2} \\ (\pi_5-\pi_6)/\sqrt{2} \end{cases} \end{aligned} \qquad (1)$$

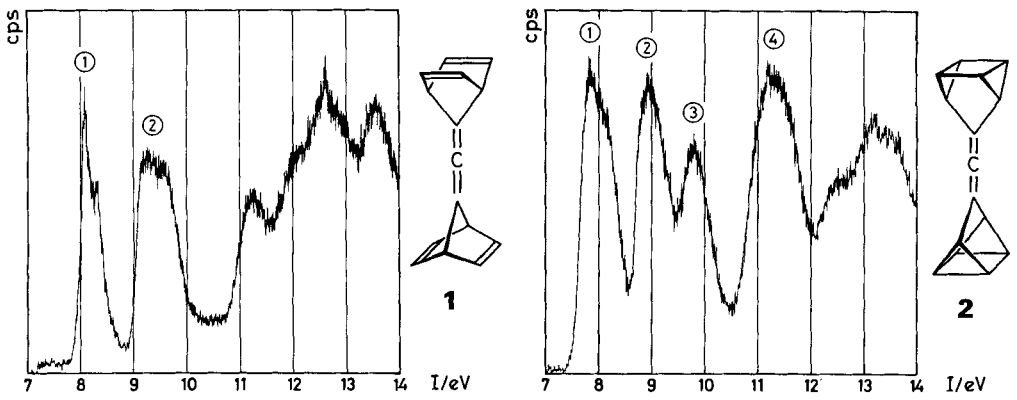


Fig. 1. *He(Iα) photoelectron spectra of* **1** *and* **2**. The individual maxima are labeled, independent of the number of bands which they contain.
Hydrocarbon **1**: $I_1^m = 8.0_5$ eV (shoulder at 8.3_0 eV); $I_2^m = 9.3$ eV (shoulder at 9.6 eV); $I_3^m = 11.3$ eV.
Hydrocarbon **2**: $I_1^m = 7.8_0$ eV (shoulder at 8.1_5 eV); $I_2^m = 8.9_5$ eV; $I_3^m = 9.7_5$ eV; $I_4^m = 11.2_5$ eV.

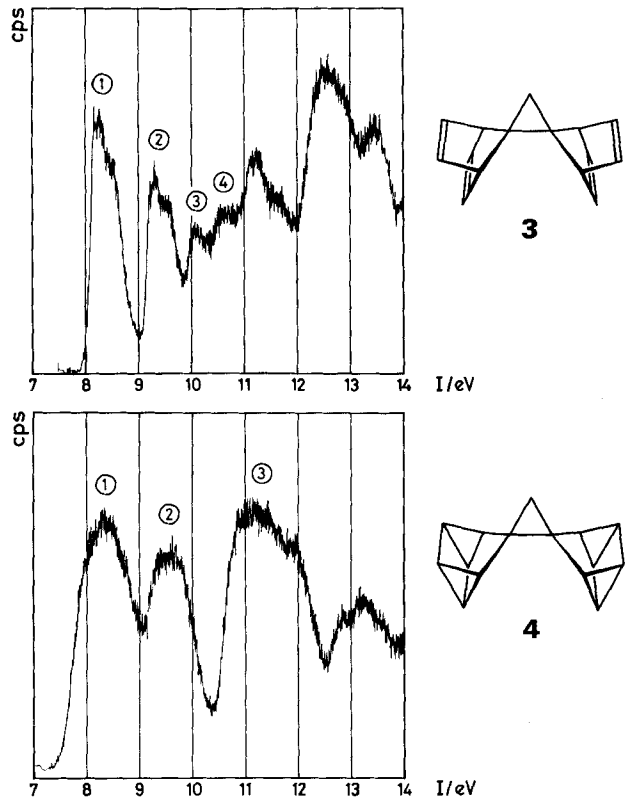


Fig. 2. *He(Ia) photoelectron spectra of* **3** *and* **4**. The individual maxima are labeled, independent of the number of bands which they contain.
Hydrocarbon **3**: $I_1^m = 8.2_5$ eV (shoulder at 8.5 eV); $I_2^m = 9.3_0$ eV (shoulder at 9.5_5 eV); $I_3^m = 10.0_5$ eV; $I_4^m \approx 10.6$ eV; $I_5^m = 11.2$ eV.
Hydrocarbon **4**: $I_1^m = 8.4$ eV; $I_2^m = 9.6$ eV; $I_3^m \approx 11.3$ eV.

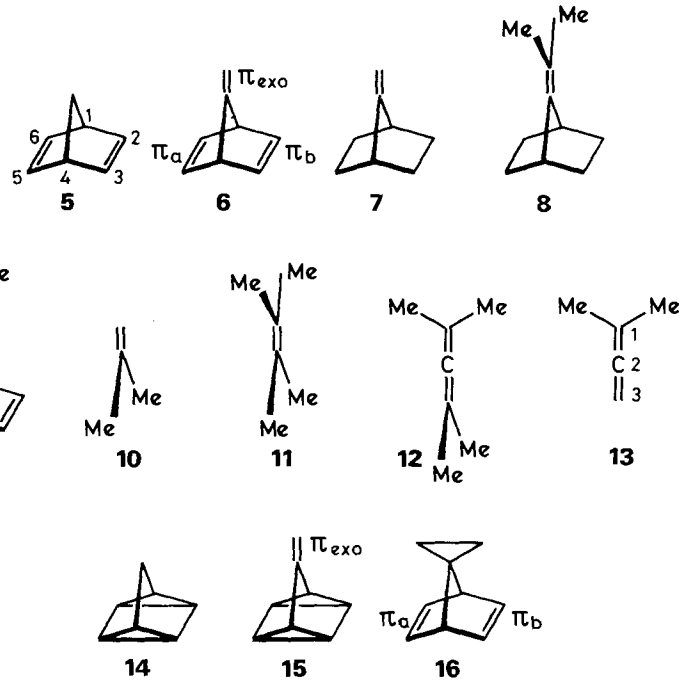
The symbols $\pi_S^u(\pi_S^l)$ and $\pi_A^u(\pi_A^l)$ represent the symmetric (S=in-phase) and antisymmetric (A=out-of-phase) linear combinations of the upper (lower) orbitals π_1, π_2 and π_3, π_4 of the norbornadiene moieties. The two degenerate pairs of orbitals e(nBD) and e(All) refer to the norbornadiene (nBD) and the allene parts (All) respectively.

Because of the lack of through space interaction within the pairs π_S^u, π_S^l and π_A^u, π_A^l the basis energies of a_1, b_2 and of e(nBD) are equal to those of the π_A and π_S semi-localized orbitals. The energies of the latter in 7-methylidene-norbornadiene (**6**) have been estimated by *Schweig et al.* [5] to be identical to those in norbornadiene (**5**) (*i.e.* $\varepsilon(\pi_A) = -8.7_0$ eV; $\varepsilon(\pi_S) = -9.5_5$ eV [6]), or perhaps shifted by -0.1 eV towards lower energies. Such a shift is also suggested by subsequent results derived from the photoelectron spectra of 7-isopropylidene-norbornadiene (**9**) [7].

To assess the orbital energies of the linear combinations e(All) we first note that the analysis of the photoelectron spectra of **6** [5] and **9** [7] yields the result

that the basis orbital energies of the two centre π-orbitals of the exocyclic double bonds in position 7 are shifted by -0.3 eV relative to the π-energies deduced in *Koopmans'* approximation from the first ionization energies $I_1 = 9.4$ eV of **7** [5] and $I_1 = 8.5$ eV of **8** [7] respectively. On the other hand a comparison of the ionization energies of **7** (9.4 eV) with $I_1 = -9.2_5$ eV of isobutene **10** [8], and of **8** (8.5 eV) with $I_1 = 8.2_5$ eV of tetramethyl ethylene **11** [8] shows that the replacement of two geminal methyl groups by a 7-norbornylidene moiety increases the π-ionization energies by 0.15 and 0.25 eV, respectively. This corresponds to a mean shift of -0.2 eV for the relevant π-orbital energy. Combining these results with the observed ionization energy $I_c = 8.6$ eV (= position of the centroid of the *Jahn-Teller* split band; $I_1 = 8.47$ eV, $I_2 = 8.96$ eV) of tetramethyl-allene **12** [9], leads to an estimate of -9.1 eV for the basis energy of the e(All) orbitals in **1**. (Note that the value I_c of the centroid is shifted by 0.1 eV relative to the mean of I_1 and I_2, because of the higher intensity of the first maximum.)

Finally we need the cross-term between the two E-type linear combinations e(nBD) and e(All). From an analysis of the photoelectron spectra of **6** [5] and **9** [7] in terms of through-space interaction [10] it was found that the homoconjugative interaction between the linear combination $\pi_A = (\pi_a - \pi_b)/\sqrt{2}$ of the two endo double bonds and the orbital $\pi_{exo} \equiv \pi_c$ of the exocyclic double bond has a value of $\langle \pi_A | H | \pi_{exo} \rangle = \sqrt{2}\, B_{endo,exo} = -0.64$ eV. Assuming that the geometry in the neighbourhood of centre 7 and that the dihedral angle of the norbornadiene system(s) are the same in **1** as in **6** or **9**, one finds that $\langle e(nBD) | H | e(All) \rangle = \langle \pi_A | H | \pi_{exo} \rangle = -0.64$ eV.



Using the basis energies derived above, *i.e.* $A(e(nBD)) = -8.8$ eV, $A(e(All)) = -9.1$ eV, and their interaction matrix element -0.64 eV, together with $A(a_1) = A(b_2) = A(\pi_S) = -9.5_5$ eV one obtains (in *Koopmans'* approximation) the following interpretation of the photoelectron spectrum of **1**:

Band	Orbital	Calc. energy	Type	Obs. ioniz. energy
①	e①	−8.29 eV	0.78 e(nBD) − 0.62 e(All)	~8.2 eV
②	a_1	−9.55 eV	a_1	9.2 ÷ 9.7 eV
	b_2	−9.55 eV	b_2	
	e②	−9.61 eV	0.62 e(All) + 0.78 e(nBD)	

(2)

This result and its genesis is shown diagramatically in *Figure 3* (left), which is self-explanatory. (The numbers in circles, which follow orbital labels of same symmetry behaviour, refer to the corresponding maxima of *Fig. 1* and *2*.)

Note that the first band ①, predicted to be of E-type, shows the typical shape of a *Jahn-Teller* envelope, albeit with reduced split (~0.2 eV), as expected in view of the spread of the orbital e① over the whole system. The broad band system, in the energy range from ~9.2 eV to ~9.7 eV has an integrated intensity twice that of band ①, in agreement with expectation based on our model. Finally, all the bands corresponding to π-ionization are collected in the first two maxima, which are followed by a large gap before the band at 11.3 eV is reached. This band is

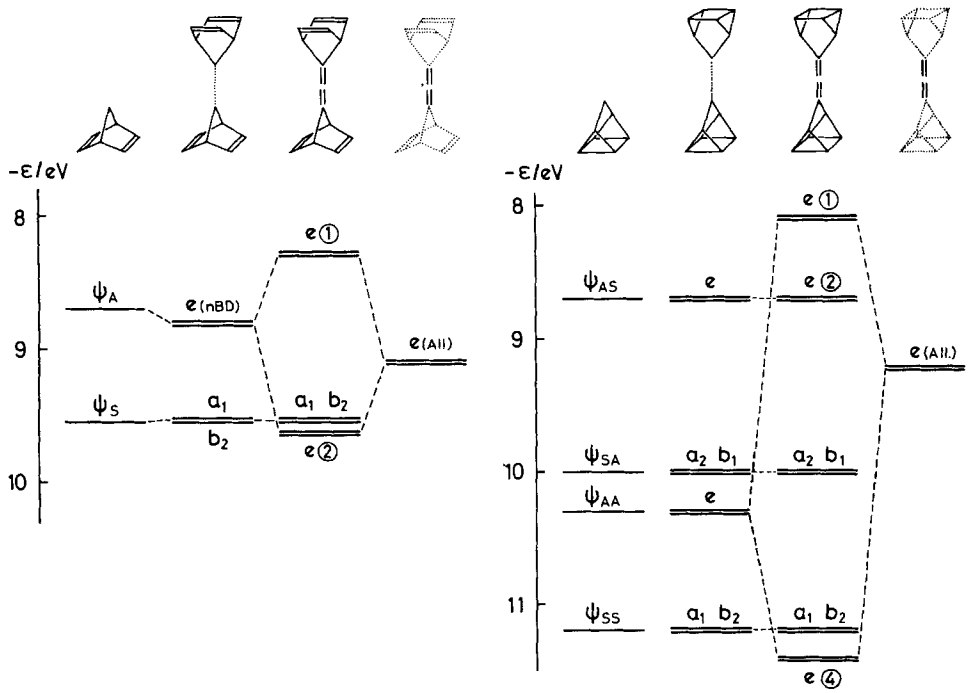
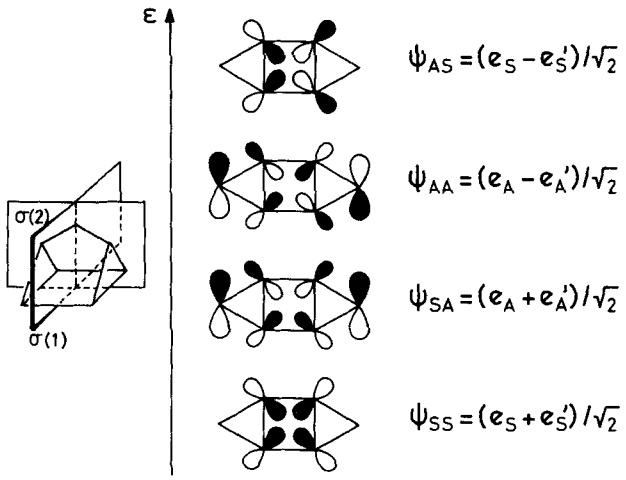


Fig. 3. *Orbital correlation diagrams:* a) Left side: *Hydrocarbon* **1** (*cf.* (2)). b) Right side: *Hydrocarbon* **2** (*cf.* (5)).

found at the same position as the first σ-band in the spectrum of **6** [5], which makes its assignment unambiguous. Apart from the relative order of the individual bands corresponding to a_1, b_2 and e② within the broad feature ②, the proposed assignment of the low energy part of the photoelectron spectrum of **1** rests on solid grounds.

Hydrocarbon 2. – The photoelectron spectrum of quadricyclane (**14**) has been recorded and assigned by *Martin et al.* [11] (see also [12]). They have shown that the first four bands ($I_1 = 8.5_5$ eV; $I_2 = 9.9$ eV; $I_3 = 10.2_5$ eV; $I_4 = 11.1$ eV [12]) can be assigned to states of the radical cation $\mathbf{14}^+$ in which one of the orbitals ψ_{AS}, ψ_{AA}, ψ_{SA} or ψ_{SS} is singly occupied. (The sequence postulated in [12] is ψ_{AS}, ψ_{SA}, ψ_{AA}, ψ_{SS}; for reasons given below we prefer to interchange the close-lying central orbitals ψ_{SA}, ψ_{AA}.) These molecular orbitals are, to a good approximation, linear combinations of the appropriate *Walsh*-orbitals of the three-membered rings of **14** which are qualitatively depicted in the following 'folded-out' diagrams borrowed from [11]:



(3)

The individual *Walsh* orbitals e_S, e_A are defined as linear combinations of 2p atomic orbitals ϕ_μ, *i.e.* $e_S = (\phi_2 - \phi_3)/\sqrt{2}$, $e_A = (2\phi_1 - \phi_2 - \phi_3)/\sqrt{6}$, and the pairs of indices of the linear combination refer to the symmetric (S) or antisymmetric (A) behaviour of the ψ relative to the mirror planes $\sigma(1), \sigma(2)$ of **14**. *Martin et al.* [11] have assigned basis energies to the above linear combinations, which have been successfully used to interpret the photoelectron spectrum of 3-methylidene-quadricyclane (**15**). However, in view of the revised data given in [12] we shall use $A(\psi_{AS}) = -8.7$ eV, $A(\psi_{SA})$ or $A(\psi_{AA}) = -10.0$ eV or -10.3 eV, and $A(\psi_{SS}) = -11.2$ eV *i.e.* the observed negative vertical ionization energies, shifted by -0.1 eV for reasons given in [11]. Whereas *Martin et al.* [11] favour the sequence $A(\psi_{SA})$ above $A(\psi_{AA})$ for the two close lying states, our results (see below for **2** and **4**) tend to indicate the reverse, namely $A(\psi_{AA}) = -10.0$ eV, $A(\psi_{SA}) = -10.3$ eV. In view of the uncertainties involved, both sequences remain valid working hypotheses.

From the semi-localized orbitals ψ_{AS}, ψ_{SA}, ψ_{AA} and ψ_{SS} of the upper and of the lower quadricyclane moieties of **2** (symmetry D_{2d}) one obtains the following symmetry conditioned linear combinations, to which the semilocalized e(All)-orbital of the allene unit has to be added:

		Basis energy	
e(AS)=	$\begin{cases}(\psi^u_{AS}+\psi^l_{AS})/\sqrt{2}\\(\psi^u_{AS}-\psi^l_{AS})/\sqrt{2}\end{cases}$	− 8.7 eV	
b_1(AA)=	$(\psi^u_{AA}+\psi^l_{AA})/\sqrt{2}$	− 10.0 eV	
a_2(AA)=	$(\psi^u_{AA}-\psi^l_{AA})/\sqrt{2}$		
e(SA)=	$\begin{cases}(\psi^u_{SA}+\psi^l_{SA})/\sqrt{2}\\(\psi^u_{SA}-\psi^l_{SA})/\sqrt{2}\end{cases}$	− 10.3 eV	(4)
a_1(SS)=	$(\psi^u_{SS}+\psi^l_{SS})/\sqrt{2}$	− 11.2 eV	
b_2(SS)=	$(\psi^u_{SS}-\psi^l_{SS})/\sqrt{2}$		
e(All)=	$\begin{cases}(\pi_1+\pi_2)/\sqrt{2}\\(\pi_1-\pi_2)/\sqrt{2}\end{cases}$	− 9.2 eV	

Because of the large spatial separation of the two quadricyclane systems in **2**, the through space interaction within each pair ψ^u and ψ^l (of same symmetry behaviour) is practically nil, so that the basis energies of the above linear combinations (4) are the same as those of the corresponding ψ-functions (3), *e.g.* A(e(AS)) $\equiv$ A(ψ^u_{AS}) $\equiv$ A(ψ^l_{AS}), *etc.* Thus the values listed for the latter are carried over for the discussion of the photoelectron spectrum of **2**, as indicated in the right column of (4).

Martin et al. have argued that the basis energy of the π-orbital π_{exo} of the exocyclic double bond in **15** is A(π_{exo}) = − 10.3 eV, *i.e.* 0.2 eV above the π-orbital energy of ethylene (− 10.5 eV). In addition to this shift we have to take into consideration the hyperconjugative destabilization of the allene π-orbitals due to interaction with the two C,C-single bonds emanating from centre 3 of each quadricyclane unit. The shift in basis energy due to this destabilization can be deduced from the two π-ionization energies observed for 1,1-dimethylallene (**13**), *i.e.* $I_1 = 8.9_5$ eV, $I_2 = 9.8_5$ eV [9]. Whereas I_1 reflects the destabilization of the π-orbital of the double bond between C(1) and C(2), by the two geminal methyl groups in position 1, the value $I_2 = 9.8_5$ eV pertains to the π-orbital of the double bond between C(2) and C(3), which is shifted by 0.7 eV relative to that of ethylene. (For a detailed discussion see [9]). Taking both shifts into account yields the basis energy of the allene-part π-orbitals at A(e(All)) = − 10.1 + 0.2 + 0.7 = − 9.2 eV. This is practically the same value as that derived by different arguments for compound **1**, *i.e.* − 9.1 eV.

From the point of view of the overall symmetry of the system one might have expected that the degenerate pair of allene orbitals e(All) will interact with e(AS) and with e(SA). However, as is evident from the diagrams for ψ_{AS} and ψ_{SA} shown in (3) only the latter has the proper *local* symmetry for interaction with one or the other of the allene π-orbitals, ψ^u_{AS} and ψ^l_{AS} being *locally* orthogonal to π_1 and π_2 of the linear combination e(All), respectively. Furthermore, both ψ^u_{AS} and ψ^l_{AS} have coefficient zero at the position next to the point of attachment to the allene

moiety. As a consequence, the only cross-term expected is that between e(SA) and e(All), a result which considerably simplifies the analysis of the photoelectron spectrum of **2**.

As shown in [13] the cross-term between a two-centre π-orbital $\pi = (\phi_a + \phi_b)/\sqrt{2}$ and an antisymmetric *Walsh*-orbital e_A is given by $\langle \pi | H | e_A \rangle = \beta/\sqrt{3}$ with a calibrated value $\beta = -1.9$ eV. Consequently one finds that $\langle e(All) | H | e(AS) \rangle = \beta\sqrt{2/3} = -1.55$ eV, which leads, together with the basis energies listed in (4) to the following assignment for the photoelectron spectrum of **2**:

Band	Orbital	Calc. energy	Type	Obs. ioniz. energy
①	e①	– 8.11 eV	0.82 e(All) – 0.58 e(SA)	~ 8.0 eV
②	e②	– 8.7 eV	$(\psi^u_{AS} \pm \psi^l_{AS})/\sqrt{2}$	8.9_5 eV
③	$a_2; b_1$	– 10.0 eV	$a_2(AA); b_1(AA)$	9.8 eV
④	$a_1; b_2$	– 11.2 eV	$a_1(SS); b_2(SS)$	11.3 eV
	e④	– 11.39 eV	0.82 e(SA) + 0.58 e(All)	~ 11.5 eV

(5)

As in the case of **1**, *Figure 3* (right) provides instant insight, how the orbital scheme of **2** relates to those of its subsystems.

It is noteworthy that the lower intensity of band ③ *(cf. Fig. 1)* has been observed previously in the photoelectron spectrum of **15** [11] in which the band at 9.9 eV corresponding to the ejection of an electron from a ψ_{AA} orbital of the quadricyclane part (in our assignment) is also of lower intensity.

Hydrocarbon 3. – The assignment of the photoelectron spectra of **3** and **4** is a bit more involved, because of the presence of *Walsh*-orbitals which do not allow for σ/π separability, even in a first approximation. Therefore the evaluation of appropriate basis energies is not as straightforward as in the examples **1** and **2**, and thus more liable to be affected with errors than in the case of π-orbitals which are locally orthogonal to the σ-frame orbitals.

The *Walsh*-orbitals of cyclopropane, which form the degenerate pair e′ (D_{3h} symmetry) can be written in a crude approximation in terms of 2p ($\equiv \phi$) orbitals as in (6).

e′	$e_S = (\phi_2 - \phi_3)/\sqrt{2}$		C_{2v}: A_1	(6)
	$e_A = (2\phi_1 - \phi_2 - \phi_3)/\sqrt{6}$		B_2	

The photoelectron spectrum of cyclopropane [14] yields, *via* the *Koopmans'* approximation an orbital energy $\varepsilon(e') \approx -10.7$ eV, which corresponds to the position of the centroid of the first band. (This band exhibits the typical *Jahn-Teller* envelope with two maxima at 10.5 and 11.3 eV, the former being of higher intensity, so that the centroid value is closer to the position of the first maximum.)

In analogy to other alkyl substituted cyclopropane systems [15–17] the basis orbital energies $A(e_S)$ and $A(e_A)$ of the *Walsh*-orbitals in **3** and **4** are shifted towards higher energies, the shifts in energy being unequal for e_S and e_A. The analysis of the photoelectron spectrum of 7-cyclopropylidene-norbornadiene (**16**)

[15], closely related to **3**, yields $A(e_A) = -9.8_5$ eV and $A(e_S) \approx -11$ eV. The most simple-minded explanation is that the norbornadiene part exerts an inductive (and hyperconjugative) destabilization of e_A which is proportional to the square of the coefficient of ϕ_1 in the linear combination (*cf.* (6)), namely as in equation 7, where

$$A(e_A) - \varepsilon(e_A) = (-9.8_5\ \text{eV}) - (10.7\ \text{eV}) = \left(\frac{2}{\sqrt{6}}\right)^2 \delta a\,(\text{nBD}), \tag{7}$$

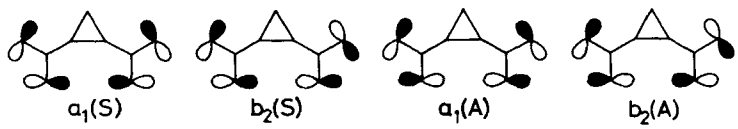
δa (nBD) is the characteristic perturbation induced by the norbornadiene part. Solving for the latter yields δa (nBD) = 1.3 eV. Using this value for the assessment of the basis energies of the *Walsh*-orbitals in **3**, one obtains the equations 8:

$$\begin{aligned} A(e_A) &= -10.7\ \text{eV} - 2\left(\frac{1}{\sqrt{6}}\right)^2 \delta a\,(\text{nBD}) = -10.3\ \text{eV} \\ A(e_S) &= -10.7\ \text{eV} + 2\left(\frac{1}{\sqrt{2}}\right)^2 \delta a\,(\text{nBD}) = -9.4\ \text{eV} \end{aligned} \tag{8}$$

Using π_S and π_A for the symmetric and antisymmetric linear combinations of the two π-orbitals of each norbornadiene system, we construct the symmetry adapted orbitals appropriate for the C_{2v} molecule **3**, where the upper indices mean l = left, r = right, and where phase relationships are defined as follows:

	Basis energies
$a_1(S) = (\pi_S^l + \pi_S^r)/\sqrt{2}$	
$b_2(S) = (\pi_S^l - \pi_S^r)/\sqrt{2}$	-9.5 eV
$a_1(A) = (\pi_A^l + \pi_A^r)/\sqrt{2}$	
$b_2(A) = (\pi_A^l - \pi_A^r)/\sqrt{2}$	-8.6 eV

(9)



(10)

The appropriate basis energies can be taken directly from [15], *i.e.* from the analysis of the photoelectron spectrum of **16**, namely $A(a_1(S)) = A(b_2(S)) = -9.5$ eV, $A(a_1(A)) = A(b_2(A)) = -8.6$ eV (*cf.* eqn. 9). (Concerning the possibility of through space interaction of the two endo double-bonds, see below.)

As in the previous case **2**, we are faced again with the fact that *local* orthogonality prohibits the interaction of $a_1(S)$ or $b_2(S)$ with either e_S (symmetry A_1) or e_A (symmetry B_2) in the molecule **3**. On the other hand, $a_1(A)$ interacts with e_S, and $b_2(A)$ with e_A, respectively.

The interaction matrix element between one of the 2p atomic basis orbital ϕ_μ, from which the *Walsh*-orbitals are constructed, and the π_A-orbital of norbornadiene, has been derived from the above mentioned analysis of **16**. Its value $\langle \phi | H | \pi_A \rangle = -0.69$ eV leads directly to the necessary cross-terms of the equations 11.

$$\begin{aligned} \langle e_S | H | a_1(A) \rangle &= -0.69\ \text{eV} \\ \langle e_A | H | b_2(A) \rangle &= -0.40\ \text{eV} \end{aligned} \tag{11}$$

Combining the basis energies of the equations 8 and 9 and cross-terms of equation 11 yields the following assignment of the photoelectron spectrum of **3** (*cf.* eqn. 12):

Band	Orbital	Calc. energy	Type	Obs. ioniz. energy
①	$a_1$①	– 8.19 eV	0.86 a_1(A) – 0.50 e_S	8.2_5 eV
	$b_2$①	– 8.51 eV	0.98 b_2(A) – 0.22 e_A	~ 8.5 eV
②	$a_1$②	– 9.5 eV	a_1(S)	9.2_5 eV
	$b_2$②	– 9.5 eV	b_2(S)	9.5_5 eV
③	$a_1$③	– 9.81 eV	0.86 e_S + 0.50 a_1(A)	10.0 eV
④	$b_2$④	– 10.39 eV	0.98 e_A + 0.22 b_2(A)	~ 10.5 eV

(12)

In *Figure 4*, left, is shown how the orbitals of **3** are related to the basis orbitals of its constituent partial systems. The agreement between calculated and observed band positions is very satisfactory (see eqn. 12) and it is obvious that the photoelectron spectrum of **3** correlates rather well with the spectra of related systems, *e.g.* **16**.

In particular there is hardly any doubt that the broad maximum ② is due to the superposition of two bands corresponding to the ejection of an electron from either a_1(S) or b_2(S), which have been assigned the same energy within our crude approximation. However, from the photoelectron spectrum it is apparent that they are split by 0.3 eV, and one might well speculate what the origin of this split is.

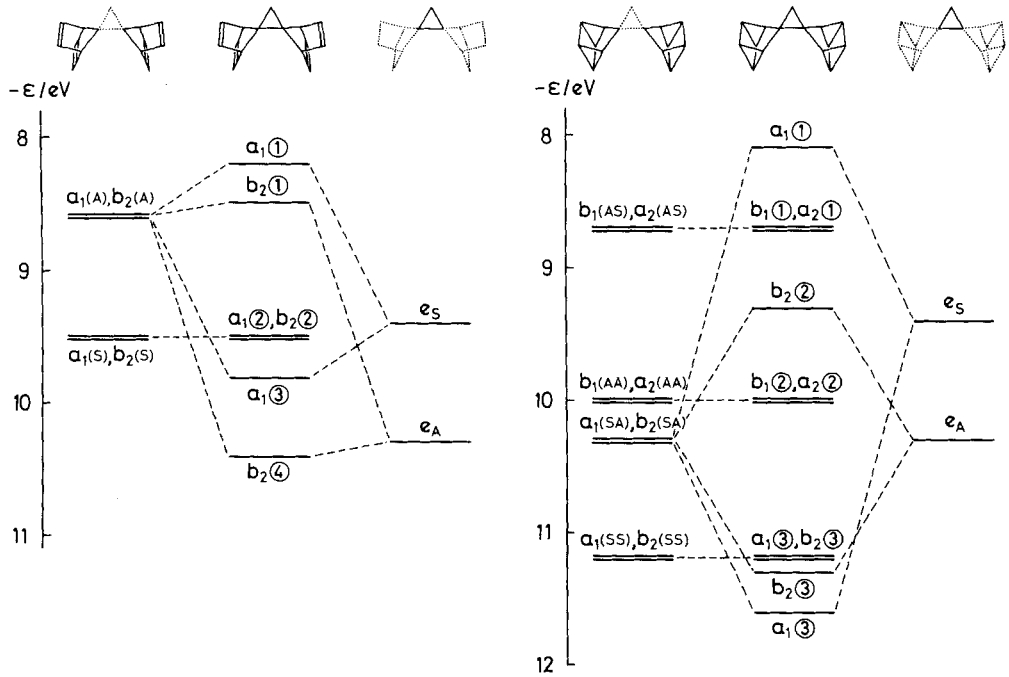


Fig. 4. *Orbital correlation diagrams:* a) Left side: *Hydrocarbon* **3** (*cf.* (12)). b) Right side: *Hydrocarbon* **4** (*cf.* (14)).

It is known from a previous theoretical treatment of **5** [18] that the 'ribbon'-orbital [19] of the six-membered ring is the relay orbital for the through bond interactions of the two π-orbitals of the norbornadiene moiety, the C,C-σ-orbitals of the bridge C(1)–C(7)–C(4) being of lesser importance. This makes it rather improbable that long-range through bond interaction is the cause of the observed split of 0.3 eV. The more probable explanation is, that it is the consequence of direct through space interaction between the endo-positioned π-orbitals, which are only $\sim$300 pm apart and thus in *van der Waals* contact. Such a value seems eminently reasonable in view of the results derived from the photoelectron spectra of cyclophanes [20] or of 1,5-cyclooctadiine [21]. If the through space mechanism is adopted, then $b_2(S)$ would be the component at lower ionization energy, *i.e.* at 9.2_5 eV.

Hydrocarbon 4. – The photoelectron spectrum of **4** consists of three broad maxima which must contain at least those ten bands which are due to the removal of an electron from the eight (= two times four) quadricyclane- and the two *Walsh*-orbitals. The former have been discussed in connection with the photoelectron spectrum of **2** (see eqn. 3) and the latter with that of **3** (see eqn. 6).

From experience we except that their basis energies are those given above in the equations 4 and 8, except for small unpredictable changes. However, we shall use them without change, if only for internal consistency.

The cross-terms between two conjugated *Walsh*-orbitals (*e.g.* in dicyclopropyl) have been deduced previously [22] and checked, using various hydrocarbons containing three-membered rings [23]. Expressed with respect to the 2p atomic orbitals ϕ_μ, which define the *Walsh*-orbitals (*cf.* equ. 8), the cross-term is $\langle\phi_l|H|\phi_r\rangle \approx -1.7$ eV, where ϕ_l and ϕ_r are the two 2p orbitals of the left (l) and right (r) cyclopropyl unit respectively, joined by a C,C-single bond.

With reference to the quadricyclane orbitals shown for **2**, we can form the following, symmetry adapted linear combinations:

$$\begin{array}{lll} & & \text{Basis energies} \\ b_1(AS)=(\psi^l_{AS}+\psi^r_{AS})/\sqrt{2} \\ a_2(AS)=(\psi^l_{AS}-\psi^r_{AS})/\sqrt{2} & \Big\} & -8.7\text{ eV} \\ b_1(AA)=(\psi^l_{AA}+\psi^r_{AA})/\sqrt{2} \\ a_2(AA)=(\psi^l_{AA}-\psi^r_{AA})/\sqrt{2} & \Big\} & -10.0\text{ eV} \\ a_1(SA)=(\psi^l_{SA}+\psi^r_{SA})/\sqrt{2} \\ b_2(SA)=(\psi^l_{SA}-\psi^r_{SA})/\sqrt{2} & \Big\} & -10.3\text{ eV} \\ a_1(SS)=(\psi^l_{SS}+\psi^r_{SS})/\sqrt{2} \\ b_2(SS)=(\psi^l_{SS}-\psi^r_{SS})/\sqrt{2} & \Big\} & -11.2\text{ eV} \end{array} \qquad (13)$$

Of these only $a_1(SA)$ and $b_2(SA)$ can interact with e_S and e_A respectively, all others being either symmetry forbidden or *locally* orthogonal to the *Walsh*-orbitals, as shown for clarity in the diagrams of *Figure 5*.

The cross-terms for allowed interactions are:

$$\langle a_1(SA)|H|e_S\rangle = \sim -1.7\text{ eV}$$
$$\langle b_2(SA)|H|e_A\rangle = \sim -1.0\text{ eV}$$

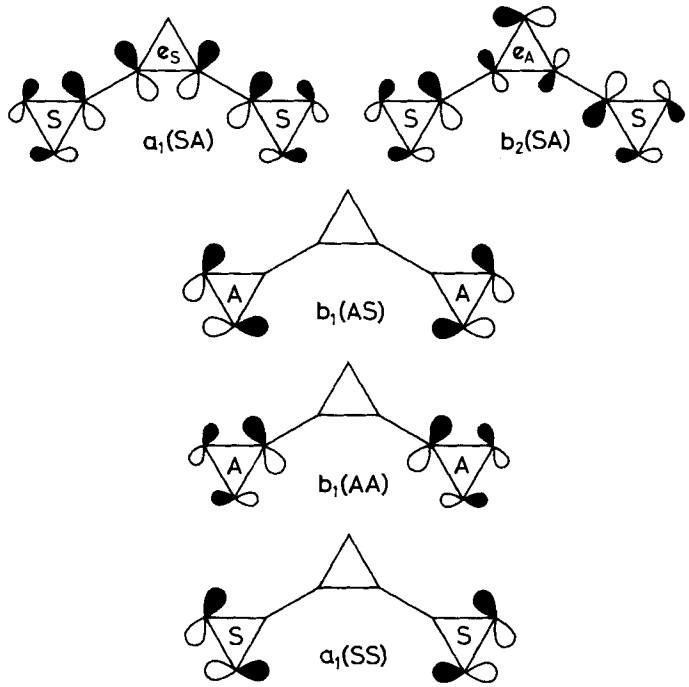


Fig. 5. *Schematic side-view of linear combinations (13).* The symbols S and A indicate if the quadricyclane orbital is symmetric or antisymmetric with respect to the plane of the paper, which contains the central *Walsh*-orbital of the cyclopropane unit. Only the two top-most linear combinations a_1(SA) and b_2(SA) can interact with e_S and e_A respectively. All the others (*cf.* (13)), of which three examples are shown (b_1(AS); b_1(AA); a_1(SS)) are orthogonal by symmetry or locally orthogonal (a_1(SS); b_2(SS)) to e_S and e_A.

This yields the following assignment, for which the corresponding orbital sequence is presented in *Figure 4*, right.

Band	Orbital	Calc. energy	Type	Obs. ioniz. energy
①	$a_1$①	– 8.09 eV	$0.79\,e_S - 0.61\,a_1$(SA)	~ 8.4 eV
	$b_1$①	– 8.7 eV	b_1(AS)	
	$a_2$①		a_2(AS)	
②	$b_2$②	– 9.3 eV	$(b_2(SA) - e_A)/\sqrt{2}$	~ 9.6 eV
	$b_1$②	– 10.0 eV	b_1(AA)	
	$a_2$②		a_2(AA)	
③	$a_1$③	– 11.2 eV	a_1(SS)	~ 11.3 eV
	$b_2$③		b_2(SS)	
	$b_2$③	– 11.3 eV	$(b_2(SA) + e_A)/\sqrt{2}$	
	$a_1$③	– 11.61 eV	$0.79\,a_1(SA) + 0.61\,e_S$	

(14)

This result is nicely compatible with the observed spectrum. However, in view of the unresolved, wide maxima it is not possible to derive any information concerning the sequence of the individual bands within any of these features.

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